



MOLECULAR FOUNDRY USER MEETING



AUGUST 11–12, 2016

Abstract Booklet

Breakout Symposia

August 12, 2016 | 9:00 am to 5:00 pm

Biological and Soft Material Assemblies

Building 54, Room 130 (Perseverance Hall)

Organizers: Ron Zuckermann, Caroline Ajo-Franklin, Bruce Cohen

9:00 am

Discovery of Affinity Reagents from Combinatorial Libraries of Functionalized Peptoid Nanosheets

Mark Kline, Berkeley Lab

Co-authors: Jae Hong Kim, Elissa M. Grzincic, Samuel C. Kim, Mohsen Karbaschi, Joshua Cardiel, Lisa Yun, Michael D. Connolly, Adam R. Abate, Ronald N. Zuckermann

The design and synthesis of protein-like polymers having hierarchical chemical diversity is a fundamental challenge in materials science. Our recent work has led to sequence-defined peptoid polymers that precisely fold into protein-like nanosheet structures. The nanosheets span areas greater than 100 μm^2 , and display a high density of chemically diverse peptoid and peptide loops on their surface. We aim to mimic the biological immune system by creating vast combinatorial libraries of these synthetic folded nanostructures, and screen them for binding to various chemical and biological targets. In order to achieve this, we use Foundry expertise in solid-phase combinatorial peptoid synthesis and supramolecular assembly, along with droplet-based microfluidic technology to produce and screen the libraries. We will present how this system was used to identify highly-selective protein-binding nanosheets. This platform is of great interest to the Dept. of Defense in order to rapidly identify and neutralize chemical and biological threat agents.

9:30 am

Computational Design of Self-Assembling Protein Nanomaterials

Jorge Fallas, University of Washington

Synthetic protein sequences designed using computational algorithms exhibit interesting properties differentiating them from their natural counterparts such as idealized geometries and high thermal and chemical stability. These characteristics make them attractive building blocks for the bottom-up fabrication of novel materials. Throughout evolution, the self-assembly of protomers into structures exhibiting high symmetry has emerged as a powerful tool to pattern biomacromolecules at the nano- and mesoscale. This approach serves as a roadmap to harness the desirable properties of the new synthetic proteins we currently have access to. I will describe a computational pipeline aimed at designing self-assembling protein oligomers programed to adopt target symmetry and discuss recent methodological advances in the field. We use our methodology to design interfaces onto idealized repeat proteins that direct their assembly into complexes with cyclic, tetrahedral, octahedral, icosahedral and helical symmetry. The designs were characterized using size exclusion chromatography, multiple-angle light scattering, small angle X-ray scattering and X-ray crystallography and transmission electron microscopy in order to confirm that they adopt the desired oligomerization state and target symmetry. Finally, I will discuss our efforts to functionalize these soft nanostructures with inorganic materials with the goal of generating bionanocomposites with novel mechanical, optical and electronic properties.

10:00 am

Biological Recognition of f-element Complexes: From Spectroscopic Probes to Therapeutics

Rebecca Abergel, Berkeley Lab

From the danger posed by potential contamination of individuals with radioactive fission products after a nuclear accident to the therapeutic use of short-lived alpha-emitting isotopes for cancer treatment, the solution chemistry of actinides has become increasingly relevant to a number of applied problems. Understanding the fundamental bonding interactions of selective f-element assemblies presents a rich set of scientific challenges and is critical to the characterization of transuranic actinide coordination chemistry in environmentally and biologically relevant species and to the development of highly efficient separation reagents or new therapeutic agents. Our approach to these challenges uses a combination of biochemical and spectroscopic studies on both in vitro and in vivo systems to characterize the selective binding of actinide ions by natural and biomimetic hard oxygen-donor architectures and the subsequent macromolecular recognition of the resulting actinide assemblies displayed by protein-based metal transport systems.

10:30 am – Break

11:00 am

Nanoscale Insights Into Microscale Combat; Mechanisms of Interbacterial Warfare

Joseph Mougous, University of Washington

We previously demonstrated a method for generating discretely structured protein nanotubes from the simple ring-shaped building block, homohexameric haemolysin co-regulated protein (Hcp). Our design exploited the observation that the crystal lattice of Hcp1 contains rings stacked in a repeating head-to-tail pattern. High-resolution detail of the ring-ring interface allowed the selection of sites for specific cysteine mutations capable of engaging in disulfide bond formation across rings, thereby generating stable Hcp nanotubes. In this presentation, I will revisit these efforts, as well as describe unexpected insights into the function of Hcp that they provided. Finally, I will discuss recent progress made toward defining the physiological significance of Hcp as a substrate of the type VI secretion system.

11:30 am

Self-Assembling Protein Nanosheets for Selective Metal Recovery

Marimikel Charrier, Berkeley Lab

Surface layer (S-layer) proteins form a highly ordered crystalline, yet porous, layer on the outermost cell surface of most species of bacteria and archaea. S-layers not only provide the cell a layer for protection, they are postulated to mediate several functions such as cell adhesion, drug resistance, and providing a scaffold for mineralization. Upon heterologous expression, these S-layer proteins self-assemble into a 2D nanosheets that are thermostable and extremely robust. This biomaterial provides an ideal scaffold to display proteins of interest. We've shown that S-layer proteins from *Geobacillus stearothermophilus* expressed with an attached metal-binding moiety are still able to crystallize into nanosheets. Furthermore, our engineered variants can bind zinc or gadolinium, depending on the attached moiety, more tightly and more selectively than the native counterpart. Therefore engineered S-layer nanosheets can unite the affinity, selectivity, and robustness needed to act as a low-cost, selective,

and reusable metal adsorbent. Based on this research, one can imagine a number of applications that this biomaterial could fill by attaching proteins with different functions to the S-layer scaffold.

12:00 pm

Accessing New Supramolecular Assemblies Through de Novo Peptide Designs

Ryan Spencer, UC Irvine

Co-author: Allon Hochbaum

The self-assembly of peptides and proteins into higher-ordered structures is encoded in the amino acid sequence of each peptide or protein. Understanding the relationship between amino acid sequence, the assembly dynamics, and structure of well-defined peptide oligomers expands the synthetic toolbox for these structures. Here, we present the X-ray crystallographic structure and solution behavior of de novo peptides that form antiparallel coiled-coil hexamers (ACC-Hex) by an interaction motif neither found in nature nor predicted by existing peptide design software. The design principles for forming these assemblies will be discussed along with the attempts to further control supramolecular assembly through residue modulation. Higher-ordered fibril assemblies derived from ACC-Hex oligomer units will also be discussed.

Making, Measuring and Manipulating Two-Dimensional Matter

Building 70A, Room 3377

Organizers: Adam Schwartzberg, Nathan Hohman

9:00 am

Two-Dimensional Crystal Growth and Polymorphism in Metal Sulfides

Zafer Mutlu, UC Riverside

Co-author: Cengiz S. Ozkan

The ability to grow crystals of a desired form is a crucial aspect of the design of new functional materials. The crystals grown in the form of two-dimension with atomic thickness possess many unique physical and chemical properties, which are dramatically distinct from their bulk counterparts, due to the quantum confinement effects. The control and characterization of the polymorphic phases in the two-dimensional crystals, where polymorphism exist, are also additional elements in the design of new materials. This talk discusses two-dimensional crystal growth of metal sulfides including tin sulfides and iron sulfides with various polymorphic phases via chemical vapor deposition. Detailed characterization of each polymorphic phase of the metal sulfides crystals is performed using several microscopy and spectroscopy methods, and the results are corroborated by ab-initio density functional theory calculations.

9:30 am

A Novel Approach for Fabricating Nano Devices Based on Transition Metal Dichalcogenides

Christoph Kastl, Berkeley Lab

Co-authors: Christopher T. Chen, Tevye Kuykendall, Shaul Aloni, Adam M. Schwartzberg

Interest in transition metal dichalcogenides (TMDs) has been renewed since the discovery of emergent properties when reduced to single two-dimensional layers. A major bottleneck to this research is the lack of reproducible and large scale synthetic methods for high quality, consistent TMD samples. We present recent advances at the Molecular Foundry in establishing a novel, scalable and highly versatile method for TMD synthesis: high quality transition metal oxide films are deposited by atomic layer deposition. Then, the deposited transition metal oxide films are transformed into TMD films by a chemical chalcogenization process. This process can be utilized to realize a variety of device structures ranging from quasi one-dimensional wires to complex three dimensional geometries. In particular, we demonstrate the fabrication of WS₂ and MoS₂ based 3D photonic crystals, 2D heterostructures, and quasi 1D nanowires.

10:00 am

Molecular Transport in Membranes Made by Stacking 2D Graphene Oxide Nanosheets

Baoxia Mi, UC Berkeley

Co-authors: Sunxiang Zheng, Casey Finnerty

Graphene and its derivatives as exemplary 2D nanomaterials have great promise as building blocks to make new nanostructured membrane materials with exceptional mechanical, electrical, chemical, and biological properties, thereby significantly improving the separation efficiency of water purification and desalination membranes. In this talk, I will present results from our ongoing research on graphene oxide (GO) membranes made by layer-stacking and bonding of appropriately spaced 2D GO nanosheets. Compared with today's widely used polymeric membranes, GO membranes are fabricated by facile methods using inexpensive carbon materials and have a fundamentally different separation mechanism. Most important, GO membranes exhibit many appealing properties such as high water permeability, excellent selectivity, multifunctionality, and superior fouling resistance. Additionally, the carbon-walled transport channel in GO membranes are believed to contribute to enhanced removal of organic molecules, thus it is very important to understand the unique molecular transport in the 2D GO nanochannels. At the end, I will point out several outstanding challenges in manipulating the nanostructure of GO membranes to maximize their desalination capability.

10:30am – Break

11:00 am

2D Crystals for Smart Life

Kaustav Banerjee, UC Santa Barbara

The experimental demonstration of graphene in 2004 has opened up a window to the two-dimensional (2D) world of materials. This has subsequently triggered a surge of research activities on various 2D crystals including single layers of hexagonal-boron nitride (h-BN), several dichalcogenides (such as MoS₂ and WSe₂), and complex oxides, with novel electronic properties. Atomic scale thicknesses (few Å/layer) of 2D semiconducting crystals and their controllable precise band gaps as a function of number of layers also enable the scaling of electronic devices without inducing performance variations. Moreover, seamless planar synthesis and stacking of 2D crystals on various substrates can be exploited to build novel lateral and vertical heterostructures, respectively. This talk will highlight and discuss the prospects of such 2D crystals and their heterostructures for designing ultra-low power, low-loss, and ultra-energy-efficient active and passive devices targeted for designing next-generation green electronics needed to support the emerging paradigm of Internet of Everything. More specifically, this talk will examine the genesis of the power dissipation challenge in conventional MOSFETs, and provide an overview of the recently demonstrated 2D-channel tunneling transistor from my group (Nature, 2015) that overcomes this challenge and is a fundamentally different transistor employing several innovations. This talk will also bring forward some other applications uniquely enabled by 2D crystals, including sensors and flexible radio-frequency electronics for improving quality of life, and discuss related challenges and opportunities.

11:55 am

Graphene Membranes for Atmospheric Pressure Photoelectron Spectroscopy

Robert Weatherup, Berkeley Lab

Co-authors: Baran Eren, Yibo Hao, Hendrik Bluhm, Miquel Salmeron

Understanding the chemical state of nanoparticle catalysts under realistic reaction conditions is of crucial importance in designing catalyst systems with improved activity and selectivity. To this end, X-ray photoelectron spectroscopy (XPS) can provide quantitative, surface sensitive information on the chemical composition of surfaces/interfaces but is normally limited to high vacuum measurement conditions. Here we demonstrate atmospheric pressure XPS using single-layer graphene membranes as photoelectron-transparent barriers that sustain pressure differences in excess of 6 orders of magnitude[1]. The membranes are produced by transferring graphene grown by chemical vapour deposition (CVD)[2,3] onto metal coated (Au or Al), perforated silicon nitride grids using a polymer-free transfer technique[1]. The suspended graphene then serves as a support for catalyst nanoparticles under atmospheric pressure reaction conditions (up to 1.5 bar), where XPS allows the oxidation state of Cu nanoparticles and gas phase species to be simultaneously probed. We thereby observe that the Cu²⁺ oxidation state is stable in O₂ (1 bar) but is spontaneously reduced under vacuum. We demonstrate the detection of

various gas-phase species (Ar, CO, CO₂, N₂, O₂) in the pressure range 10-1500 mbar including species with low photoionization cross-sections (He, H₂). We expect this graphene membrane approach to be a valuable tool for studying nanoparticle catalysis under atmospheric pressure reaction conditions, as well as a promising technique for studying solid-liquid interfaces during electrochemical reactions.[4]

- (1) Weatherup et al. J. Phys. Chem. Lett. 2016, 7, 1622–1627
- (2) Weatherup et al. J. Am. Chem. Soc. 2015, 137, 14358–14366
- (3) Weatherup et al. J. Am. Chem. Soc. 2014, 136, 13698–13708
- (4) Velasco-Velez et al. Angew. Chemie Int. Ed. 2015, 54, 14554–14558

Structural and Functional Diversity in Porous Soft Materials

Building 2, Room 100B

Organizers: Yi Liu, David Prendergast

9:00 am

Electrochemical CO₂ Reduction Over Precisely Fabricated Metal Organic Frameworks and Covalent Organic Frameworks”

Yingbo Zhao, UC Berkeley

Conformal and oriented metal-organic frameworks thin films are fabricated with precisely controlled thickness and pristine interface. This is achieved by atomic layer deposition of aluminum oxide on the substrates and addition of a tetra-topic porphyrin based linker, 4,4',4''-(porphyrin-5,10,15,20-tetrayl)-tetrabenzic acid (H₄TCPP), to react with alumina and make MOF [Al₂(OH)₂TCPP] enclosures. Alumina thickness is precisely controlled from 0.1 to 3 nm, thus allowing control of the MOF thickness from 10 to 50 nm. Electron microscopy and grazing angle X-ray diffraction confirm the order and orientation of the MOF by virtue of the porphyrin units being perpendicular to the substrate surface. When metalated with cobalt, the Al₂(OH)₂TCPP-Co thin film functions as catalyst for the selective and efficient reduction of carbon dioxide to carbon monoxide (CO) in aqueous electrolytes with a selectivity for CO beyond 76% and stability over 7 h with a per-site turnover number (TON) of 1400. This electrochemical catalytic activity is unique to the thin film form of the MOF (below 100 nm) and depends strong on the film thickness. This research presents a generalizable method to produce structurally well-defined nano-MOF composite material that has extraordinary functions. A parallel approach that incorporates the same Co-TCPP catalytic motif in to covalent organic frameworks also produced efficient electrocatalyst with extraordinary TOFs and demonstrated potential synergistic effects between the framework backbone and the catalytic motif that lead to superior catalytic properties.

9:30 am

Investigating Nanostructured Organic Frameworks and Porous Polymers with X-ray Scattering

Michael Brady, Berkeley Lab

Porous soft materials are ideal platforms for carbon dioxide sequestration, selective gas separators, Li-S battery membrane components, and matrices for functional nanocomposites. In a structural sense, in all of these applications the pore size and morphology, tortuosity, and directionality are critical parameters, and this talk will focus on the use of x-ray scattering tools to characterize the pores in covalent organic frameworks (COFs) and polymers of intrinsic microporosity (PIMs). The ability to solution process COFs into organized sheets of individual framework polymers in the form of thin films presents enormous flexibility, and here wide angle x-ray scattering and absorption spectroscopy are used to reveal the superior control of pore texture in thin films following solution growth. In addition, the use of both wide and small angle x-ray scattering as tools for studying the porous nanostructure of PIMs are highlighted, both for the study of intermolecular spacing of the rigid backbone units, as well as morphology and tortuosity. A novel method of blending surface-treated nanoparticles into PIMs to manipulate the nanocomposite structure will be presented.

10:00 am

The Importance of a Precise Crystal Structure for Simulating Gas Adsorption in Nanoporous Materials

Keith Lawler, University of Nevada, Las Vegas

We show that simulation of gas adsorption in nanoporous sorbents may be highly sensitive to accurate crystallographic coordinates, even for frameworks anticipated to have low flexibility. Using HKUST-1, a material generally regarded as rigid, we compared carefully collected experimental noble gas adsorption isotherms and GCMC simulations carried out with 12 experimentally determined evacuated and gas loaded crystal structures to illustrate the under-appreciated and often overlooked detail in the community: even small differences in crystallographic descriptions of a framework can lead to appreciable changes in predicted isotherms. We also performed molecular dynamics simulations of HKUST-1 at two temperatures and various loadings of noble gas to further illustrate how the framework changes during adsorption. For additional emphasis, we will compare the initial selectivities. Additionally, we will analyze the predicted gas adsorption selectivities across a wide range of thermal conditions.

10:30 am – Break

11:00 am

Electrohydrodynamic-assisted Assembly of Hierarchically Structured, 3D Graphene Monoliths for Efficient Energy Harvesting and Solar Conversions

Vincent Tung, UC Merced

Graphene emerges as a tantalizing candidate for next generation energy harvesting and storage despite its short history. Its transformation into crumpled graphene-nanoparticles (CGNs) is expected to decouple the layer-dependent material properties from bulk processing. In this talk, we will demonstrate the use of electrohydrodynamic assembly as a scalable, low temperature, template-free and versatile means to synthesize CGNs. This strategy conceptually mimics charge-stabilized colloidal systems that concurrently introduce electrostatic and capillary stimuli, initiating stages of self-propelling, fission and anisotropic compression of individual graphene into hierarchically functional CGNs. We demonstrate that when assembled collectively, structurally adaptable CGNs progressively self-assemble into monolithic foam with hierarchical topography that comprises high yields of single-layered graphitic membranes structurally supported by folded plateau. When integrated individually, high aspect ratio architecture inherent in CGNs can be repurposed as vertically-propagated and energetically-favorable transport layers. Further, the synthetic strategy can be used as a massively parallel design principle for unprecedented 3D crumpled transitional metal dithalogenides, unlocking new inroads into enhancing catalytic properties.

11:30 am

The Computation-Ready Experimental Metal-Organic Framework Database: Development and Applications

Jeffrey Camp, Georgia Institute of Technology

Metal-organic frameworks (MOFs) are a class of crystalline nanoporous materials with record surface areas and unique pore geometries. Computational screening of the over 5,000 experimentally reported MOF structures can streamline efforts to identify materials suitable for applications ranging from gas storage to chemical sensing. These computational screening efforts depend on simulation-ready crystallographic information for each structure. Prior to this work, the availability of simulation-ready crystal structures is a major impediment to applying high-throughput computations to MOFs because experimentally refined structures include artifacts such solvent molecules that significantly decrease porosity. The central result of this work is the public availability of a nearly comprehensive set of MOF structures that are derived directly from experimental data but are immediately suitable for molecular simulations. As an example of using our CoRE MOF database, we have revealed relationships between structural characteristics of MOFs and performance in vehicular natural gas fuel storage.

12:00 pm

Metal-Organic Frameworks to Enable Low-Cost Distributed Chemical Sensors

David Britt, Matrix Sensors

As connected devices proliferate in our society we have begun to view each node as a "bundle of sensors" that generates a stream of data we can use to understand and control our lives. The list of ubiquitous sensors, which now includes accelerometers, thermometers, microphones, and cameras among others, continues to grow. From this list chemical sensors are notably absent. Their omission owes to a combination of faults, including cost, size, power requirement, and longevity. We aim to take advantage of the unique class of metal-organic framework (MOF) materials to establish a platform technology for low-cost chemical sensing. I will discuss the advantages offered by MOFs in this domain, as well as the technical obstacles that remain and our efforts to overcome them.

Tackling Challenges of Imaging Materials Functionality: Symposium on current imaging technology & workshop on future and current needs at the Molecular Foundry

Building 50 Auditorium

Organizers: Peter Ercius, Francesca Toma, Alex Weber-Bargioni

9:00 am

Cathodoluminescence at the Movies: Revealing Nanoscale Dynamics in Solid and Liquid Solutions

Naomi Ginsberg, Berkeley Lab and UC Berkeley

Cathodoluminescence (CL) images map the nanoscale luminescent properties of materials as a function of the location of a rastering electron beam. Although the use of CL imaging with metallic or inorganic materials is common, its application to more delicate materials is far more limited since they are susceptible to extensive damage from typical electron beam exposures. I will nevertheless give examples of the ways that my research group has extended CL imaging to more delicate—and even dynamic—solids and solutions by substantially minimizing direct electron exposure. We perform all of our experiments in the Foundry Zeiss Supra SEM, where we have worked with Oglethorpe, Aloni, Barnard, and Wong to achieve high efficiency light collection, low-exposure and rapid frame or movie collection, and optical and thermal control. As an example of resolving dynamics in solid materials, I will describe the movies that we obtained to visualize both thermally- and photo-induced phase transitions in mixed halide hybrid perovskites. In conjunction with David Limmer's multiscale simulations we have elucidated the origin of this latter effect to be due to polaronic lattice strain. I will argue that nonequilibrium processes in many other hybrid materials, e.g. in MOFs or nanocrystal superlattices, may be explored with similar approaches. To observe solution-phase dynamics without running a current through the liquid, we developed CL-activated imaging: imaging of a sample using its local resonant electromagnetic interaction with a nearby electron-beam-excited volume in a thin scintillating film. I will show movies of the thermally-induced formation of hybrid perovskite films in addition to the motions of small particles in ionic liquids and oils, with a view toward capturing biomolecular interactions under physiological conditions.

9:30 am

Facet-Dependent Photovoltaic Efficiency Variations in Perovskite Grains

Sibel Leblebici, Berkeley Lab

Co-authors: Linn Leppert, Yanbo Li, Sebastian E. Reyes-Lillo, Francesca M. Toma, Jeffrey B. Neaton, Ian D. Sharp, Alexander Weber-Bargioni

Microscopic structure and orientation of the perovskite crystals affect performance parameters such as photocurrent generation and open-circuit voltage. These performance parameters are difficult to quantify on the nano-scale and as a result are generally considered homogeneous within perovskite films. We mapped short-circuit photocurrent and open-circuit photovoltage in MAPbI₃-xCl_x films and MAPbBr₃ microstructures using conductive atomic force microscopy. These measurements reveal significant facet-dependent heterogeneity in short-circuit current and open-circuit voltage due to surface trap states. These results provide key insights

to enhance device performance of both polycrystalline and single crystal photovoltaic devices.

10:00 am

First Principles Modeling of Structural and Electronic Properties of Hybrid Halide Perovskites

Linn Leppert, Berkeley Lab

Co-author: Jeffrey B. Neaton

Solar cell devices based on hybrid halide perovskites have reached efficiencies of more than ~20% owing to the appealing optoelectronic properties of these materials. First principles calculations have played a major role in increasing the understanding of the physical properties that underlie this remarkable efficiency. However, density functional theory (DFT), the workhorse of modern computational materials science, faces a range of challenges when dealing with hybrid halide perovskites. Most notably, the organic moiety, e.g., methylammonium (MA), is believed to rotate freely in room and high temperature phases of MAPbI₃, an effect generally disregarded in static DFT calculations. The electronic structure, and in particular properties that can be relevant for the material's transport characteristics, such as effective masses and the so-called Rashba effect, depend sensitively on the assumed orientation of the MA moieties. Similarly, the rotational freedom of the molecules has to be taken into account, when mapping structural properties like lattice parameters or atomic distances to experimental results. In my talk, I will present our recent efforts to address these challenges, by elucidating the coupling between electric polarization, which increases as a function of the macroscopic alignment of the MA moieties, and electronic structure properties that are experimentally accessible. In particular, our calculations show that effective masses increase as a function of polarization, an effect that might explain the dark current heterogeneity recently observed in MAPbI₃ thin films using scanning probe microscopy (1). The Rashba effect, an energy band splitting in k-space, also increases with increasing polarization, and can be tuned by chemical substitution of the MA molecule and anisotropic strain (2). Finally, I will show an ad hoc "pseudatom" approach that allows replacement of MA in calculations with minimal loss of accuracy, leading to excellent agreement with experiments for lattice parameters and Pb-halide bond lengths for mixed halide perovskites.

(1) S. Leblebici, L. Leppert, et al., Facet-dependent photovoltaic efficiency variations in single grains of hybrid halide perovskites, *Nature Energy* 1, 16093 (2016).

(2) L. Leppert, S. E. Reyes-Lillo, J. B. Neaton, Electric field and strain induced Rashba effect in hybrid halide perovskites, in preparation (2016).

10:30am – Break

11:00 am

Spatial Mapping of 2D Valence Bands at the MAESTRO Beamline at ALS

Eli Rotenberg, Berkeley Lab

Recently, the MAESTRO beamline has been commissioned for the study of in situ grown materials by angle-resolved photoemission spectroscopy (ARPES) with simultaneous spatial- and energy-resolution at the ALS. The beamline consists of PEEM, microARPES, and nanoARPES analysis endstations, which have complementary spatial resolutions from 10 micron to (in principle) 50 nm, coupled to chambers for sample preparation by MBE, PLD, and micromechanical exfoliation. I will give an overview of the facility capabilities, including the initial experimental results of the electronic structure of 1- to few-layer 2D transition metal dichalcogenides (2DTMDs), and other 2D materials.

11:30 am

Probing Properties of Matter at the Nanoscale by Scanning Electron Nanodiffraction

Roberto dos Reis, Berkeley Lab

The scattering of a finely focused electron beam traversing a thin foil provides rich information about the sample such as structure, composition, phonon spectra, three-dimensional defect crystallography and more. Rastering the beam to record these convergent beam electron diffraction (CBED) patterns at many positions with milliseconds dwell times enables many types of images from a single experiment. Such a four-dimensional dataset is comprised of a 2D CBED pattern at each point in a 2D STEM raster image, namely 4D-STEM. In this presentation, I will describe applications of 4D-STEM technique to reveal materials properties at the nanoscale. Examples will be given on probing polarization in doped HfO₂ ferroelectric films, identification of point defects and octahedral rotations in

halide perovskites. Additionally, strategies to extract multiple information from such large datasets, as well as some of the issues on data processing, will be addressed.

12:00 pm

Imaging of Biomolecules and Bioinspired Materials at the Molecular Foundry

Paul Ashby, Berkeley Lab

The Molecular Foundry has many resources for imaging biological, bio-inspired, and soft organic materials. In-situ Atomic Force Microscopy (AFM) offers high spatial resolution on order of a nanometer for imaging the organization of protein complexes and the ability to monitor large-scale conformational dynamics. I will present the Foundry's efforts to improve spatial and temporal resolution with the development of encased cantilevers and high speed scanning techniques.

1:30 pm

The Future of TEM is Faster, with Clearly More Data to Analyze"

Andy Minor, Berkeley Lab and UC Berkeley

There is an ongoing revolution in the development of electron detector technology that has enabled modes of electron microscopy imaging that had only before been theorized. The age of electron microscopy as a tool for imaging is quickly giving way to a new frontier of multidimensional datasets to be mined. These improvements in electron detection have enabled cryo-electron microscopy to resolve the three-dimensional structures of non-crystallized proteins at 2.2Å— potentially revolutionizing structural biology and four-dimensional reciprocal space maps of materials at atomic resolution, providing all the structural information about nanoscale materials in one experiment. With direct detectors the complexity and scale of electron microscopy is now beginning to approach particle physics and astronomy as a data intensive science. This talk will highlight advances in thin film nanomechanics, atomic resolution tomography and a new method of imaging enabled by direct electron detectors, where a series of 2D diffraction patterns are collected at each position in a 2D STEM raster scan resulting in a four-dimensional data set. For thin film analysis, direct electron detectors hold the potential to enable strain, polarization, composition and electrical field mapping over relatively large fields of view, all from a single experiment.

2:00 pm

Advanced Low Energy Electron Microscopy to Image Functional Materials

Andreas Schmid, Berkeley Lab

One powerful advantage of microscopy with visible light is that these probes can be so gentle: even fragile materials often survive investigation unharmed. Electron microscopy can provide far greater resolution, but as the probe energy – usually many thousands of eV – greatly exceeds chemical bond energies – no more than a few eV – many materials suffer radiation damage. How about making electron probes that are as gentle as, say, sunshine in the morning? Energy of photons making up a pretty sunrise is of order 1eV. Electrons with energy 1eV have 1000 times shorter wavelength than those photons, and this provides powerful opportunities for low energy electron microscopy. Low energy electrons reflected off surfaces are exquisitely sensitive to the physical properties of functional materials Molecular Foundry researchers are developing. This talk will outline several examples, including microscopic imaging of work function and patch fields, mapping the orientation of the magnetization vector, electrical potentials, and chemical composition. We will also highlight opportunities provided by cutting edge instruments, including damage-free imaging of biological and biomimetic materials at spatial resolution that permits measurements such as sequencing unlabeled DNA just by imaging the molecule.

2:30 pm

Quasi-Operando Imaging of the Surface Structure-Product Selectivity Functionality of Electrocatalysts by Seriatim ECSTM-DEMS

Manuel Soriaga, California Institute of Technology

Co-authors: Youn-Geun Kim, Alnald Javier, Jack H. Baricuatro

It is known that the structure of a well-ordered electrocatalyst surface can be determined under quasi-operando conditions by electrochemical scanning tunneling microscopy (ECSTM). It is also recognized that the product distribution of a catalytic reaction can be monitored by differential

electrochemical mass spectrometry (DEMS). It may thus be expected that the combination of DEMS and ECSTM would deliver a unique hyphenated technique that is able to identify, under actual reaction conditions, the particular surface-structural feature that gives rise to a given product selectivity. We recently implemented seriatim (sequential) ECSTM-DEMS in the study of the regulation of the Cu-catalyzed electrochemical reduction of CO to generate a single product via the atomic-level structural modification of the Cu surface. This will be the subject of the presentation.

3:00 pm – Break

3:30 pm

Three Dimensional Localization of Nanoscale Battery Reactions Using Soft X-ray Tomography

David Shapiro, Berkeley Lab

Battery function is determined by the efficiency and reversibility of the electrochemical phase transformations at solid electrodes. The spectro-microscopic tools available to study such transformations with the required spatial resolution and chemical specificity are intrinsically limited when studying complex architectures by their reliance on two-dimensional projections of thick material. Here, we report the development of soft X-ray ptychographic tomography, which resolves chemical states in three dimensions at 11-nm spatial resolution. We study an ensemble of nano-plates of lithium iron phosphate (LiFePO₄) extracted from a battery electrode at 50% state of charge. Using a set of nanoscale tomograms, we quantify the electrochemical state and resolve phase boundaries throughout the volume of individual nano-particles. These observations reveal multiple reaction points and intraparticle heterogeneity that highlights the importance of electrical connectivity, providing critical insight to the design of the next generation of high-performance devices.

4:00 pm

First-principles interpretation of X-ray spectral imaging

David Prendergast, Berkeley Lab

We will explore the strong connection between interpretation of images and necessary modeling of the imaged phenomena. Even for homogeneous systems, interpretation of X-ray spectra can be challenging, often requiring computationally intensive first-principles approaches. However, for systems with nanoscale inhomogeneity the challenge is even greater and stretches us to the limits of computational feasibility. We will provide examples from the field of scanning transmission X-ray microscopy (STXM) where there is evidence for phase coexistence in nanoscale domains of battery materials and our efforts to explain those observations. We will also outline future possibilities based on recent operando X-ray spectral measurements taken on electrochemical cells that will surely benefit from complementary nanoscale imaging. 4:30 pm

4:30 pm

Through a Flask, Darkly: Imaging Needs from a Chemical Perspective

Jeff Urban, Berkeley Lab

Performing atom-precise syntheses with phase purity and quantitative conversion is a crown jewel on the throne of chemistry and chemical engineering. However, at present, few reactions approach this limit, and the vast majority of chemical processes run in the lab suffer from unexpected side products and poor conversion; moreover the reasons underpinning these non-idealities often remain opaque to the synthetic scientist. In this talk I'll describe a wishlist of imaging modalities that span the plausible but difficult to the purely hypothetical that offer the potential to provide key insights into how to overcome historical challenges in synthesis and deliver enhanced functionality in materials creation.

Energy Storage Materials: Synthesis, Characterization and Modeling

Building 70A, Room 3377

Organizer: Alpesh Shukla

1:30 pm

Composite of Two-Dimensional Titanium Carbonitride “MXene” and Nano-Sulfur as Cathode for Li-S Batteries

Michael Naguib, Oak Ridge National Laboratory

Co-author: Jagjit Nanda

Few years ago, a new family of two-dimensional, 2D, transition metal carbides and carbonitrides called MXenes were produced for the first time by etching atomically thin metal layers from ternary layered materials called MAX phases. The latter have a composition of $M_nA_nX_n$, where M stands for early transition metal, A is a metal that belongs to groups 13 and 14 in the periodic table, X is carbon/nitrogen, and $n = 1, 2$, or 3. With more than 15 different compositions (e.g. Ti_3C_2 , Ti_3CN , V_2C , Nb_2C , Mo_2C) synthesized so far, MXenes can be considered as the fastest growing family of 2D materials. In addition to their chemical compositions versatility, MXenes offer unique combinations of properties. For example, they have high electrical conductivity and they exhibit hydrophilic behavior, which is a rare combination of properties in layered materials. In this presentation, the recent progress in the synthesis of MXenes, understanding their structure, and exploring their properties will be summarized. Their performance in energy related applications (e.g. Li- and beyond Li-ion batteries, and supercapacitors) will be discussed in details.

2:00 pm

Crystal-Based Microscopy and Spectroscopy Diagnostics for Lithium-ion Battery Cathode Development

Guoying Chen, Berkeley Lab

Co-authors: Saravanan Kuppan and Alpesh K. Shukla

Lithium transition-metal oxides (Li-TM oxides) are presently the most promising cathode materials for high-energy lithium-ion batteries. When operated at high voltages (>4.3 V) in battery cells, however, these oxides suffer from structural instability, extensive side reactions with the electrolyte, poor cyclability and severe thermal runaway reactions. In order to develop successful strategies to address these issues, there is a clear need in fundamental knowledge of oxide crystal structures, cycling-induced phase transformation and surface reactions on the cathode. To this end, a unique diagnostic approach combining carefully prepared cathode model samples and the start-of-the-art analytical techniques with high spatial resolution and chemical specificity was developed in our lab. In this presentation, we will discuss the synthesis of Li-TM oxide crystals with specific sizes and morphologies. Through the use of complementary microscopy and spectroscopy techniques at multi-length scale, including aberration corrected (scanning) transmission electron microscopy, electron energy loss spectroscopy, X-ray energy dispersive spectroscopy, full-field transmission X-ray microscopy and X-ray absorption near edge structure imaging, surface sensitive soft X-ray absorption spectroscopy and X-ray photoelectron spectroscopy, we reveal a range of heterogeneities in atomic-level structure, elemental and chemical distributions on pristine particles. Combined with in situ and ex situ electrochemical analyses, we discuss the impact of the heterogeneities on electrochemical performance, the key factors influencing side reactions at the cathode/electrolyte interface, and the phase transition mechanism during Li extraction/reinsertion.

2:30 pm

Electronic Structure, Entropic and Quantum Effects in Nanoscale Aqueous Systems

Tod Pascal, Berkeley Lab

Co-author: David Prendergast

A fundamental understanding of the properties of water molecules next to 2-D interfaces is critical for rational design of future aqueous energy storage devices. Recent efforts have focused on nanoscale, graphene-based materials, where the large solid/liquid contact surface area and extreme "hydrophobicity" would elicit phenomena not seen in conventional systems. Yet the thermodynamics of such systems, as it relates to the role of entropy in the intrinsic interfacial stability, has not been explored. We present results from extensive computer simulations that uniquely quantifies the molecular entropy and quantum corrections to the enthalpy of water in contact with graphene and graphite. We explore the effect of nanoscale confinement on the system thermodynamics and demonstrate

how fluctuations at the interface induces nonlinear effects that leads to the stabilization of the second water layer. Finally, we propose that interfacial waters possess a unique electronic structure, as probed by vibrational and X-ray absorption spectroscopies. These results are contrasted with that of water at platinum and gold electrodes.

2:45 pm

Effect of Non-Uniform Porosity on Lithium Plating

Sun Ung Kim, Robert Bosch Research and Technology Center

Co-author: Abdul-Kader Srouji, Jake Christensen

A postmortem analysis on aged-prismatic cells demonstrated that the lithium plating is spatially non-uniform; however, exact causes of the lithium plating was not clear. Two-dimensional electrochemical model has been developed for investigating how non-uniform porosity affects lithium plating. Two factors should be considered for the lithium plating simulations, however: (1) in compressed regions, the ionic resistance of electrolyte would be lower because the thickness is smaller; (2) the effective electrolyte diffusion will be slower because of the lower porosity in the region. The 2-D simulation results showed that the dominating factor in the system might be the electrolyte diffusion.

3:00 pm – Break

3:30 pm

NMC Cathode and LLZO Electrolyte Studies

Marca Doeff, Berkeley Lab

Co-authors: Feng Lin, Lei Cheng, Chixia Tian, Dennis Nordlund, Huolin Xin

Li-ion batteries have reached a high level of performance, but more is required from them if widespread electrification of vehicles is to become a reality. Advanced materials such as Ni-rich NMC cathodes and ceramic electrolytes based on $Li_7La_3Zr_2O_{12}$ (LLZO), which may enable use of lithium metal anodes, could allow energy densities in excess of 250 Wh/kg to be obtained, but there are questions about thermal and interfacial stability. This talk will cover the author's recent work on NMC and LLZO materials designed to answer these questions, emphasizing synchrotron techniques as well as advanced microscopy.

4:00 pm

TiS₂/CNT Hybrid Supercapacitors-battery Breaks the Limit of Supercapacitors Based on Aqueous Electrolyte

Xining Zang, UC Berkeley

Co-authors: Caiwei Shen, Weihua Cai, Emmeline Kao, Ruopeng Zhang, Kwok Sion Teh, Aiming Yan, Yingxi Xie, Adam Schwartzberg, Liwei Lin

We design and develop both the electrode and electrolyte to address a new energy storage system with high energy and high power density. TiS_2 is the cheapest and lightest sulfate in the transition metal di-chalcogenide (TMDC) family, with the highest energy storage potential as lithium-ion battery anode material. In this paper, TiN coated onto carbon nanotube (CNT) by atomic layer deposition is converted to TiS_2 annealing in sulfur vapor flow. Combining the high surface area and high conductivity induced by CNT and the interlayer ion storage of TiS_2 , the hybrid material results in a specific capacitance of $\sim 500F/cm^3$ (roughly 500F/g). We introduce the salt lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) which has only been applied in Li^+ battery before in aqueous supercapacitors, and prove a working voltage of 3 V which not only breaks the water splitting limit of 1.23 V but also power the energy density up to 625 Wh/kg. Cyclic voltammetry test of TiS_2/CNT LiTFSI cell shows the character of supercapacitors, while TiS_2 intercalation with Li^+ introduce battery character instead of redox reaction in pseudocapacitors. Addressing this hybrid supercapacitor-battery, highest power density and energy density based on aqueous electrolyte. LiTFSI, the water in salt electrolyte is also dissolve in PVA/H₂O gel to make semi solid state electrolyte for device assembly. Flexible supercapacitors-battery based on the LiTFSI with symmetric double electrode performs at 2.5 V with a high device projection capacitance of $\sim 60mF/cm^2$.

4:15 pm

Discussion: Future of energy storage research

Playing with Photons at the Nanoscale

Building 54, Room 130 (Perseverance Hall)

Organizers: *Stefano Cabrini, Jim Schuck*

1:30 pm

Hot Electron and Surface Plasmon Drive Chemical Reactions

Jeong Y. Park, Korea Advanced Institute of Science and Technology

A pulse of high kinetic energy electrons (1–3 eV) in metals can be generated after surface exposure to external energy, such as the absorption of light or exothermic chemical processes. These energetic electrons are not at thermal equilibrium with the metal atoms and are called “hot electrons”. The detection of hot electrons and understanding the correlation between hot electron generation and surface phenomena are challenging questions in the surface science and catalysis community [1-3]. Hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) appears to be correlated with localized surface plasmon resonance. In this talk, I will show the research strategy to develop the energy conversion devices based on the hot electron. To detect and utilize the hot electron flows, the nanodiodes consisting of metal catalyst film, semiconductor layers, and Ohmic contact pads were constructed. It was shown that the chemicurrent or hot electron flows were well correlated with the turnover rate of CO oxidation or hydrogen oxidation separately measured by gas chromatography, suggesting the intrinsic relation between catalytic reaction and hot electron generation [4]. We showed that the direct conversion of photon energy to the hot electron flows can be achieved in metal-semiconductor nanodiodes. We showed that hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) is amplified by localized surface plasmon resonance [5]. New concept of tandem structured- hot electron photovoltaic cell gave rise to higher energy conversion efficiency [6]. I will also discuss the new architecture of hot electron collections using graphene based nanodiodes [7,8]. Finally, The effect of surface plasmons on the catalytic and photocatalytic activity on metal–oxide hybrid nanocatalysts is also highlighted. These phenomena imply the efficient energy conversion from the photon energy to the chemical energy, with the potential application of photocatalytic devices.

[1] H. Lee, I. I. Nedrygailov, C. Lee, G. A. Somorjai and J. Y. Park, *Angewandte Chemie* 54, 2340 (2015)

[2] J. Y. Park, L. R. Baker, and G. A. Somorjai, *Chemical Reviews* 115, 2781-2817 (2015)

[3] J. Y. Park, S. M. Kim, H. Lee, and I. I. Nedrygailov, *Accounts of Chemical Research* 48, 2475-2483 (2015)

[4] I. I. Nedrygailov et al. *Angewandte Chemie* (in press, 2016).

[5] Y. K. Lee et al. *Nano Letters*, *Nano Letters* 11, 4251 (2011)

[6] Y. K. Lee et al. *Scientific Reports* 4, 4580 (2014)

[7] Y. K. Lee et al. *Scientific Reports* 6, 27549 (2016).

[8] H. Lee et al. *Nano Letters*, 16, 1650–1656 (2016).

2:05 pm

Probing Sub-5 nm Gap Plasmon Using Collapsible Nano-fingers

Boxiang Song, University of Southern California

Co-authors: *Yuhan Yao, He Liu, Yifei Wang, Yuanrui Li, Stefano Cabrini, Adam Schwartzberg, Stephen Cronin, Wei Wu*

In this work, we successfully fabricated gap plasmonic structure with precisely controlled sub-5 nm nano-gaps by using collapsible nano-fingers. Based on these structures, we have proved how plasmonic enhancement can change with gap size, tunneling barrier and light polarization at such a small scale when electron-tunneling effect becomes significant.

2:25 pm

Campanile-Inspired 3d Near Field Optical Probes

Alexander Koshelev, aBeam Technologies

Campanile near field probe is a novel type of nano-optical tips which can efficiently convert photonic mode into sub diffraction plasmonic hot spot. These tips have been successfully used for hyperspectral imaging of nanostructures with nanoscale resolution, providing so far in-accessible insights into optoelectronic process¹⁻³. The key to the success of the campanile tips is their efficiency in delivering light to the subdiffraction hot spot. Unfortunately, this efficiency drops with the increase in campanile size. This presents an opportunity to further improve excitation and collection efficiency, because campanile probes are usually fabricated on the edge of single mode fibers with relatively large mode field diameter of 4

µm. Here present two novel near field probe designs that are inspired by campanile structure, but with significant improvement on the light conversion efficiency. The first structure is a pin-wheel design, which looks similar to the campanile structure only with more sides. Even though the structure is similar, the underlying optical effects are different. In particular, the pin-wheel structure works for both polarizations, as opposed to the campanile, which transmits only one. The second approach is a hybrid photonic - plasmonic structure consisting of a diffractive optical element and a small size campanile. The diffractive optical element converts the large fiber mode into the field distribution at the input size of the campanile. After that, campanile, due to its small size, can efficiently convert light into plasmonic hot spot.

3:00 pm – Break

3:30 pm

Systematic Design in Hybrid Chalcogenides

J. Nathan Hohman, Berkeley Lab

Isolating 2D monolayers from layered van der Waals solids has been a fruitful approach for discovering new properties in old materials. For example, although layered transition metal dichalcogenides (TMDs) are typically indirect band gap semiconductors in the bulk, TMD monolayers possess direct band gaps and high electron mobilities, a consequence of isolating materials that already exhibit 2D quantum confinement. Building devices out of ultrathin materials poses a variety of technical challenges: considerable effort must be expended to ensure isolation of stable monolayers, postsynthetic modification is challenging, and integration into devices can alter the unique properties enabled by the ultrathin structure. We employ a hybrid chemical approach that combines organic and inorganic constituents in a single material, providing a route towards the preparation of 1D and 2D ultrathin materials wherein the organic ligands serve as a structural element and insulating dielectric. Here, we will demonstrate the synthesis and characterization of metal-organic chalcogenide assemblies (MOCHA), wherein ultrathin late transition metal chalcogenides are supported by a supramolecular nanostructure. Ligand design presents considerable opportunities for manipulating the optoelectronic properties of this new class of hybrid chalcogenides.

4:00 pm

Shape Approaches for Enhancing Plasmon Propagation in Grapheme

Roman Krahne, Italian Institute of Technology

Co-authors: *Mario Miscuglio, Davide Spirito, Remo Proietti-Zaccaria*

Graphene plasmonics are a promising alternative for high speed communication devices that integrate optics and electronics. A key advantage for graphene plasmons (GPs) over surface plasmons (SPs) on metal dielectric interfaces is related to the strong confinement of electromagnetic energy at sub-wavelength scales, which can be tuned and controlled via the charge carrier density through a gate voltage. A major disadvantage for graphene plasmons is related to their rather short decay length in the infrared range, due to plasmonic losses intrinsic to graphene and induced by the SiO₂ substrate. This drawback makes the realization of integrated optoelectronic devices extremely challenging. Therefore, viable approaches for launching and conveying graphene plasmons towards efficient and reliable communication on a device scale are needed. One means for overcoming this limitation is represented by the combination of graphene plasmonic waveguides and noble metal antenna. Here we discuss and analyze, using numerical simulations, different designs of metal antennae and their coupling to graphene plasmons, as well as graphene based nanopatterned waveguides that can lead to a more efficient GP propagation. The Yagi-Uda antenna design leads to stronger and more directive coupling to GP as compared to a standard dipole antenna. The combination of a Yagi-Uda antenna coupled to graphene nanowire waveguides on SiO₂ enables propagation length exceeding 3 µm and phase control of the propagating wave. Longest propagation lengths can be achieved by launching GPs with dipole antenna in tapered graphene waveguides.

4:20 pm

Energy-looping Nanoparticles: Harnessing Excited State Absorption for Deep-tissue Imaging

Emory Chan, Berkeley Lab

Near infrared (NIR) microscopy enables non-invasive imaging in tissue, particularly in the NIR-II spectral range (1000-1400 nm) where attenuation due to tissue scattering and absorption is minimized. Lanthanide-doped

upconverting nanocrystals are promising deep tissue imaging probes due to their photostable emission in the visible and NIR, but these materials are not efficiently excited at NIR-II wavelengths due to the dearth of lanthanide ground state absorption transitions in this window. Here, we develop a novel class of lanthanide-doped imaging probes that harness an energy-looping mechanism that facilitates excitation at NIR-II wavelengths, such as 1064 nm, that are resonant with excited state absorption transitions but not ground state absorption. Using computational methods and combinatorial screening, we have identified lanthanide-doped NaYF₄ nanoparticles that exhibit efficient looping and emit at 800 nm under continuous-wave excitation at 1064 nm. Using this benign excitation with standard confocal microscopy, energy-looping nanoparticles (ELNPs) are imaged in cultured mammalian cells and through brain tissue without autofluorescence. Imaging depths and features sizes are comparable to those demonstrated by state-of-the-art multiphoton techniques, illustrating that ELNPs are a promising class of NIR probes for high-fidelity visualization in cells and tissue.

4:40 pm

TiN for Improved Plasmonics with Plasma-Enhanced Atomic Layer Deposition

Lauren Otto, University of Minnesota

Co-authors: Aaron T. Hammack, Shaul Aloni, Deirdre L. Olynick, D. Frank Ogletree, Bethanie J. H. Stadler, Adam M. Schwartzberg

We demonstrate TiN as a plasmonic thin film developed with low-temperature plasma-enhanced atomic layer deposition (PE-ALD). As plasmonic applications are incorporated into industrial technologies, robust plasmonic materials deposited with commercially-viable techniques are a necessity. Traditional materials such as Ag and Au exhibit excellent plasmonic properties but both suffer from thermal and mechanical instabilities. Moreover, Ag is known for its chemical instability. The synthetic metal TiN exhibits plasmonic properties in the visible and near-infrared regions and has improved chemical, mechanical, and thermal robustness. While high quality TiN is typically produced via sputtering at high temperatures (700-800C), potential industrial applications including CMOS and heat-assisted magnetic recording (HAMR) require deposition below 400C. In addition, the ability to deposit uniformly on a variety of substrate materials and topographies is important. Using PE-ALD, lower temperature depositions are enabled, and TiN is capable of nucleating on a variety of surfaces. Furthermore, the conformal coating nature of ALD makes it uniquely suited to the fabrication of three-dimensional structures. We will share characterization from spectroscopic ellipsometry performed in situ to our TiN depositions and x-ray photoelectron spectroscopy as well as our work towards the fabrication of plasmonic nanostructures and material optimization.

Product-Driven Research at the Molecular Foundry

Building 2, Room 100B

Organizers: Kristen Aramthanapon, Brett A. Helms

1:30 pm

High-Throughput Materials Discovery for Advanced Additive Manufacturing

Raymond Weitekamp, polySpectra

polySpectra has developed a new class of modular 3D printing resins, capable of manufacturing production quality parts with tailored geometry and chemical functionality in a single step. We refer to this process as functional lithography – the ability to simultaneously define the form and function of advanced materials. The application of functional lithography to additive manufacturing enables production-ready parts to be directly 3D-printed, whereas existing materials can only make prototypes, mock-ups or toys. In collaboration with the Molecular Foundry, we have developed a high-throughput workflow to formulate, test and analyze more than 100 formulations in a single day. I will discuss how our supported proposals have enabled us to rapidly accelerate our commercialization pathway, from laboratory accident to minimum viable product.

1:50 pm

Incorporating Metal-Organic Frameworks into Electromechanical Devices for Consumer Products

David Britt, Matrix Sensors

Matrix Sensors, Inc. began its first user project at the Molecular Foundry in January 2014. Over the past 2.5 years the Foundry has played a crucial role in the company's development as it executed a pivot to developing low-cost distributed gas sensors based on metal-organic frameworks. Since that time Matrix has obtained almost \$2 million in government funding and closed an equity investment with a venture company and a strategic industrial partner. It is safe to say that the company would not exist in its present form without the Foundry. I will describe Matrix's change of direction, highlighting the unique role of the Foundry and the science performed here. I will also discuss the ways that our tenure here has contributed back to the Foundry's own scientific efforts.

2:10 pm

Towards Efficient, Scalable Electricity Generation Using Thermionic Energy Conversion

Jared Schwede, Spark Thermionics

Our goal at Spark Thermionics is to develop efficient heat-to-electricity conversion devices based on thermionic energy conversion. This technology, based on the thermal emission of electrons into vacuum, had its heyday in the 1960s, when numerous researchers reported converters with power conversion efficiencies >15%. However, following the end of the space race, thermionics has been largely forgotten. We propose that this presents an opportunity to apply decades of progress in materials and experimental techniques to reimagine and rapidly advance thermionic technology. In this talk, I discuss how our Foundry collaborations bring unique capabilities and expertise that can dramatically accelerate thermionic development. I describe our theoretical and experimental work to understand—for the first time—a major parasitic loss that had been essentially neglected in thermionic analyses.

2:30 pm

Anti-Fouling, Self-Cleaning Coatings for Heat Exchangers

Sebnem Inceoglu Yilmaz, Nano Hydrophobics

Water repelling, anti-fouling and self-cleaning coatings are of great interest both for scientific and technological reasons. Fouling is the unwanted deposition, such as calcium carbonate, which precipitate out of water due to inverse solubility with temperature, and form a layer on heat transfer surfaces. Because of their poor thermal conductivity, even thin layers of fouling cause significant reductions in the thermal efficiency of heat exchangers. Overall, fouling in heat exchangers is estimated to cost U.S. industry \$40 Billion per year. Many attempts have been made to solve the mineral fouling problem through coatings, but without commercial success. Currently, there is no heat transfer surface coating that has been adopted by industry to solve the fouling problem. Nano Hydrophobics' objective for the research at Molecular Foundry is to develop low surface energy thin film coatings, which prevent the deposition of mineral fouling on industrial heat exchanger surfaces in order to improve energy efficiency and reduce greenhouse gas emissions.

2:50 pm

Development of Metal-Organic Frameworks for Applications in Industrial Gas Separations

Thomas McDonald, Mosaic Materials

Mosaic Materials, a Cyclotron Road cohort company, is working to significantly reduce the cost and energy consumption of industrial gas separations. Through developing advanced metal-organic frameworks adsorbent materials, we are currently developing a technology suitable for acid gas separations, which will be tested in the field for biogas purification. An overview of our unique technology, which adsorbs CO₂ using a novel cooperative adsorption mechanism, will be presented. An overview of the challenges associated with the industrial use of new adsorbents will be presented alongside our efforts to demonstrate our ability to inexpensively scale metal-organic framework synthesis.

3:10 pm – Break

3:30 pm

Bio-Based Monomers for Bulk Polymer Applications

Deepak Dugar, Visolis

Abstract not available.

3:50 pm

Exosome-Tunneling Nanotube Constructs for Cellular Rescue in Neurodegenerative Diseases

Greg Maguire, BioRegenerative Sciences

Stem cell therapeutics is a powerful means to heal the human body. However, instead of cells, we use the molecules released from stem cells. Why? Because the power of stem cell therapeutics is largely the result of molecules that stem cells release (Maguire, 2013). The molecules are packaged into exosomes, a smart nanosphere that is naturally produced by the stem cells (Maguire, 2016), resulting in protection, perfusion, and delivery of the molecules in a synergistic fashion – i.e. all the molecule types are delivered to the target at the same time and in the same space, yielding synergistic, systems-level effects (Maguire, 2014). The molecules contained in the exosomes include microRNA and proteins, such as heat shock proteins, chaperones, antioxidants, growth factors, and proteasomes. For the exosomes that are released from healthy cells to rescue neurodegenerative cells, an intact extracellular matrix (ECM) is required, along with a tunneling nanotube (TNT) emanating from the cell at risk to the healthy cell. Exosomes are known to rescue neurons by, for example, delivering HSPs and chaperones to repair misfolded, prion-like proteins. Considering neurodegenerative diseases, often the ECM is dysfunctional and not permissive to the formation of TNTs to transmit the exosomes from the healthy cell to the diseased neuron, or other diseased neural cell types. Our goal is to make exosomes with attached TNTs that can be perfused into patients with neurodegenerative diseases, such that the exosomes with added TNT constructs can attach to the diseased neurons and deliver their contents for initiating cellular rescue.

4:10 pm

Functionalizable Fluorescent Nanodiamonds for Bioimaging

Joyce Wahba, Bikanta

Co-authors: Min Wang, Li Zhuo, Roger York, Ambika Bumb

Fluorescent nanodiamonds (FNDs) are biocompatible particles with indefinite photo-stability that makes them superb imaging probes that could replace commonly used optical agents for a wide range of applications. The negatively charged nitrogen-vacancy (NV^-) center is a defect in the diamond lattice consisting of a substitutional nitrogen and a lattice vacancy that form a nearest-neighbor pair. NV^- centers are fluorescent sources with remarkable optical properties including quantum efficiency near unity, indefinite photo-stability (i.e. no photo-bleaching or blinking), broad excitation spectra, and exquisitely sensitive magnetic field-dependent fluorescence emission. Bikanta uses FND magnetic sensitivity to improve visualization deeper into tissue and with more than 100-fold improvement in signal-to-background. Additionally, FNDs have long fluorescence lifetimes (~17ns) that can be used for time-gated imaging to suppress background signal from tissue autofluorescence (1-2ns). In particular, their near infrared fluorescence makes them ideally suited for in vivo imaging. However, FND use has been limited thus far because of difficulty in functionalizing or coating their inert surface and because of their tendency to aggregate. In order to overcome these challenges, we have developed a number of customizable stable coatings. Having such an optically superior, stable, and functionalizable nanoparticle essentially introduces a new building block to the fields of nanotechnology and nanomedicine. Rather than having the typical unreactive surface, they can be tightly bound to any targeting agent (e.g. aptamers, antibodies) and can therefore be tailored to detect specific diseases. There are a multitude of in vitro and in vivo applications for this unique technology, including fiducial marking, high resolution optical imaging, histology, optically detected magnetic resonance, molecular imaging, and early cancer detection.

4:30 pm

From the Arctic Ocean to Industry: X-Therma's Biomimetic Anti-Ice Nanomaterial

Xiaoxi Wei, X-Therma

Co-author: Chunhui Bao, Zackary Pieters, Ellen Robertson, John Schloendorn

X-Therma Inc. is a biomimetic nanotech company with the mission to develop safe & effective antifreeze solutions to enable long term bio-banking of Regenerative Medicine and enhance mechanical performance at extreme temperatures for greener industrial applications. Antifreeze is a

critical additive to control unwanted ice growth in a wide array of industries from medicine to the automobile industry. A major chemical breakthrough is demanded because of the limitations of the classic antifreeze, dimethyl sulfoxide and glycols, and their adverse toxicity. One of Nature's solutions is antifreeze proteins with 500-10,000x potency compared to the industrial standard antifreeze, yet we lack the ability to create a reliable commercial resource. Therefore, X-Therma created a new approach by embracing the beauty of Nature's design and the power of nanotechnology to bring a scientific solution to the world. Thanks to the Molecular Foundry User program, X-Therma has developed the first bioinspired, non-toxic and 500x more effective anti-ice nanomaterial via biomimetic nanoscience. Early proof-of-concept in high value applications has demonstrated cell preservation ability and safety. We received starting funding from the national project "Organs on Demand" initiated by the Department of Defense and followed by the White House and Department of Energy. Now, X-Therma together with the Molecular Foundry has become the representative chemical research effort and received significant research funding and traction. X-Therma material can potentially address more markets with huge potential: engine coolant/industrial heat transfer fluids, airplane deicing, and others. One important segment is to provide a greener solution to mechanical deicing and cooling. Overheating caused by low efficiency cooling and toxic decomposition of glycols is associated with >50 % of modern engine failure, especially for diesel engines and electric batteries. Incorporating X-Therma material could lead to superior antifreeze that is more eco-friendly, far more effective, and could extend to advanced mechanical designs owing to superior heat transfer options.